# Phosphorus Sorption by Sediments in a Southeastern Coastal Plain In-Stream Wetland

J. M. Novak\* and D. W. Watts

#### **ABSTRACT**

A close relationship has been reported between sediment organic C (SedOC) content and its P sorption capacity (Pmax) and total P (TP) concentration. Phosphorus sorbed to organically complexed cations is a proposed explanation for this relationship. The objectives of this study were (i) to determine relationships between in-stream wetland SedOC content and both the sediment's  $P_{max}$  and TP concentrations, and (ii) to ascertain the role of both organically complexed and oxalate-extractable cations on the sediment  $P_{\text{max}}$  and TP values. The sediment's oxalate-extractable Fe (Fe<sub>ox</sub>) and Al (Al<sub>ox</sub>) contents were determined using acidified ammonium oxalate, while sodium pyrophosphate was used to extract organically complexed cations ( $Al_{pryo}$ , Capyro, Fepyro, Mgpyro, and Mnpyro). Both the sediment's Pmax and TP contents were strongly correlated with its SedOC concentration ( $r^2 >$ 0.90, P < 0.001). Only the Al<sub>ox</sub> contents were significantly correlated with TP and P<sub>max</sub>, suggesting that amorphous Al forms have an important role in P sorption. All five pyrophosphate-extracted cations were significantly correlated with SedOC contents. Regression analyses showed that the Al<sub>pyro</sub> accounted for 88% of the variation in sediment P<sub>max</sub> values, whereas a combination of Al<sub>pyro</sub> and Ca<sub>pyro</sub> accounted for 98% of the variation in sediment TP concentrations. Additionally, Al and Ca chelated by SedOC compounds also have an important role in P binding and indicate that a linkage exists between the wetlands SedOC and Pmax content and its ability to accumulate TP. This study identified that two different mechanisms have significant roles in regulating P sorption by sediments in a southeastern Coastal Plain in-stream wetland.

WETLANDS have an important role in influencing P concentrations in streams, rivers, and estuaries along the southeastern U.S. coast (Reddy et al., 1999). Wetlands can act as a sink for P (Reddy et al., 1999; Novak et al., 2004). If wetlands are overloaded with P, however, they can release P, thereby acting as a source (Richardson, 1999; Novak et al., 2004). A wetland's P sink-source relationship is controlled by biological, physical, and chemical processes that function in the wetland's water column and underlying sediment. Biological processes (i.e., macrophytes and algae) can account for 10 to 50% of P binding in the water column and sediment pore water (Haggard et al., 1999; Richardson, 1999). On the other hand, physical and chemical processes associated with soils and sediments can bind between 80 and 90% of P that flows through wetlands (Richardson, 1999). Principal chemical features of wetland sediments that regulate P<sub>max</sub> values are pH, Fe<sub>ox</sub> and Al<sub>ox</sub> (Richardson,

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1985; Reddy et al., 1995, 1999), redox status (Golterman, 1995), and the SedOC content (McDowell et al., 2003; Hogan et al., 2004; Wang et al., 2005; Bruland and Richardson, 2006).

The involvement of Fe and Al oxides and hydroxides in P binding by wetland sediments is well established; however, the mechanism that promotes P binding by SedOC remains unclear. Phosphorus sorption by organic C (OC) structures is unlikely, because of the anionic character of both species at neutral pH (Schnitzer, 1969). Therefore, several investigators have indicated that P sorption can occur through the electrostatic attraction of P species to Al and Fe chelated by organic structures (Axt and Walbridge, 1999; Darke and Walbridge, 2000; Pant and Reddy, 2001; Hogan et al., 2004; Riggle and von Wandruszka, 2005). These studies, however, did not consider the potential involvement of other chelated cations (i.e., Ca, Mg, Mn, etc.) with P sorption. Competition between multivalent cations for the organic chelation sites may promote P sorption differences in wetland sediments. If so, then questions remain concerning the quantity and type of cations chelated by SedOC and their subsequent role in P binding.

Sodium pyrophosphate can be used to estimate cations chelated by organic structures in soils (McKeague, 1967; Bascomb, 1968; Gunjigake and Wada, 1981; Zhou et al., 1997) and in wetland sediments (Hogan et al., 2004). The relationships between a single cation type and sets of pyrophosphate-extractable cations with sediment P-binding characteristics can then be established through single or multivariant statistics. We have established a dual hypothesis: that cations complexed by SedOC will influence sediment  $P_{max}$  values; and that cations with greater ionic charge will have a stronger statistical effect (high  $r^2$ values and lower probability values) on P binding (Bowden et al., 1980; Stevenson, 1994). If a positive relationship exists between SedOC contents and sediment P<sub>max</sub> values, then a relationship may also exist between SedOC and its TP concentration. This is plausible because as the sediment's P<sub>max</sub> value increases, more P will be bound, thus contributing to the accumulation of P in the TP pool. The objectives of this experiment were to: (i) determine the relationships between SedOC contents and both P<sub>max</sub> values and TP concentrations, and (ii) ascertain the role of both organically chelated and oxalate-extractable cations on the sediment P<sub>max</sub> and TP values.

# MATERIALS AND METHODS In-Stream Wetland Description

The investigated in-stream wetland is located in the Cape Fear River Basin of Duplin County, North Carolina. Duplin

**Abbreviations:**  $Al_{ox}$ , oxalate-extractable aluminum;  $Fe_{ox}$ , oxalate-extractable iron; OC, organic carbon;  $P_{max}$ , phosphorus sorption maxima; SedOC, sediment organic carbon; TP, total phosphorus.

County is in the middle Coastal Plain physiographic region and is underlain with sandy- to loamy-textured marine sediments (Daniels et al., 1999). The land surface is nearly level to gently sloping, but includes small upland depressional areas (Daniels et al., 1999). Streams that flow through these depressional areas flood periodically, and after vegetative colonization can form in-stream wetlands. Soils in the wetland areas include the poorly to very poorly drained Coxville (fine, kaolinitic, thermic, Typic Paleaquults) and the organic-matter-enriched Johnston (coarse-loamy, siliceous, active, acid, thermic, Cumulic Humaquepts) series.

The in-stream wetland is supplied with water from a first-order, black water stream. The stream system drains a small subwatershed (~200 ha) that is under intensive agricultural production (Novak et al., 2002). The in-stream wetland has a well-defined inlet and outlet and is covered with surface water that is usually 0.2 m deep near the border areas and 2.5 m deep in sections near the inlet and outlet (Fig. 1). Grass vegetation and shrubs grow in the relatively flat shallow border areas. Irrigation and recreational requirements imposed by the owner during this study caused the size of the wetland to vary between 0.31 and 0.97 ha (Novak et al., 2004).

## **Sediment Collection and Chemical Composition**

The in-stream wetland was sectioned into thirds to yield locations at the inlet, at two sites within the wetland, and at the outlet (Sites 1–4, respectively; Fig. 1). The samples collected from the wetland are referred to as sediments instead of soils because flowing stream water deposited the material. Samples were collected annually (1997–1999) during September at the four locations (n=12). Sediments from the inlet (Site 1) and outlet (Site 4) were collected in the channel near midstream. Sediments from sites within the in-stream wetland (Sites 2 and 3) were collected in a grassy, relatively flat location covered by a shallow water depth (0.2–0.8 m deep). Sediments were collected to a 20-cm depth using a 5-cm-i.d. bucket auger containing a plastic sleeve. Residual water in the sleeve was decanted;

the samples were then transported back to the laboratory on ice. Sediments were air dried and sieved to 2 mm.

The sediment TP concentrations were determined in triplicate using the ascorbic acid method according to Greenberg et al. (1992), using a nutrient autoanalyzer. Sediment pH values were determined using a 1:2 ratio of sediment to deionized water. The SedOC contents were measured by dry combustion (Novak et al., 2004).

Organically bound cations were extracted in triplicate sediment samples using the alkaline pyrophosphate (Na<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, pH 10) method of Wada and Higashi (1976). The concentrations of five pyrophosphate-extracted cations (Al<sub>pyro</sub>, Ca<sub>pyro</sub>, Fe<sub>pyro</sub>, Mg<sub>pyro</sub>, and Mn<sub>pyro</sub>) in the filtrate were measured using an inductively coupled plasma–mass spectrometer (ICP–MS). The Fe<sub>ox</sub> and Al<sub>ox</sub> were extracted using the acidified ammonium oxalate (pH 3) method of McKeague and Day (1966) and their concentrations were also determined using ICP–MS.

# Dissolved Phosphorus Sorption and Isotherm Calculation

Phosphorus sorption was determined by shaking (18 h) triplicate tubes containing 1 g of air-dried sediment with inorganic P (made from KH<sub>2</sub>PO<sub>4</sub> and dissolved in 0.01 M CaCl<sub>2</sub>) concentrations of 0, 0.012, 0.025, 0.05, 0.075, 0.1, 0.125, and 0.15 mg L<sup>-1</sup> using a sediment/solution ratio of 1:10. Prior P sorption work with wetland sediments showed that these conditions were sufficient for equilibrium to be reached (Novak et al., 2004). After shaking, the tubes were centrifuged, and the supernatants were filtered using a 0.45-µm nylon syringe filter. The inorganic P concentrations remaining in the supernatants (equilibrium P concentration) were quantified using the colorimetric method of Murphy and Riley (1962). Phosphorus sorption was calculated as the difference between the amount of P initially added to the sediment and that in solution at equilibrium. A mean quantity of P sorbed and equilibrium P concentration was calculated for each of the 12 sediment samples.

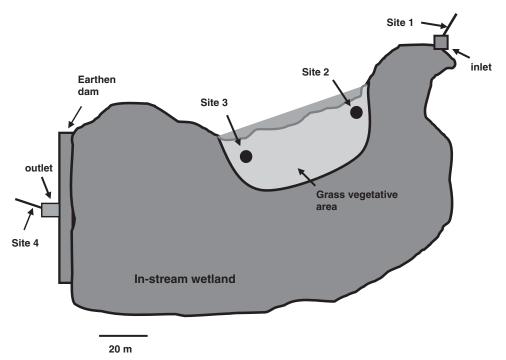


Fig. 1. Location of sediment sampling sites for the in-stream wetland.

A P sorption isotherm was constructed by plotting the quantity of P sorbed (mg  $kg^{-1}$ ) against the P equilibrium concentration (mg  $L^{-1}$ ) using the linear form of the Langmuir equation:

$$x = (1/P_{\text{max}})c + 1/(kP_{\text{max}})$$
 [1]

where x (mg kg<sup>-1</sup>) is the quantity of P sorbed by the sediment,  $P_{max}$  (mg kg<sup>-1</sup>) is the P sorption maximum, k (L mg<sup>-1</sup>) is a sorption constant relative to P bonding energy, and c (mg L<sup>-1</sup>) is the P equilibrium concentration (Olsen and Watanabe, 1957). The values of x were not corrected for previously sorbed P. The sediment sorption data fit the Langmuir equation well with all  $r^2$  values being >0.9 (data not presented). The y intercept (1/( $kP_{max}$ ) and slope (1/ $P_{max}$ ) of each isotherm were determined, and subsequently used to calculate the  $P_{max}$  values.

## **Statistical Comparisons**

The mean pH, SedOC, TP,  $P_{max}$ , and quantities of oxalate-and pyrophosphate-extractable cations from the sediments at each site were calculated from the triplicate measurements. Using the mean sediment chemical properties by site and year, simple or multiple regression analyses were used to discern the most significant relationships between TP,  $P_{max}$ , SedOC content, and quantities of oxalate- and pyrophosphate-extractable cations. An exponential rise to a maximum model was used to describe the strength of the relationship between P sorption and SedOC and P sorption with extracted cations using

$$y = a[1 - \exp(-bx)]$$
 [2]

where  $y = P_{max}$  (mg kg<sup>-1</sup>), x = SedOC (mg kg<sup>-1</sup>) or extracted cation concentration (mg kg<sup>-1</sup>), and a and b are equation parameters. This model was selected because it produced better curve-fitting results (higher  $r^2$  values and lower P values) than a parabolic model. All computations and regression relationships were determined using SigmaStat (SPSS, 2005).

## **RESULTS AND DISCUSSION**

## Chemical Characteristics of the In-Stream Wetland Sediments

Freshwater wetlands in the Carolina Coastal Plain region are OC-enriched because inflowing water has high dissolved OC concentrations (~5–7 mg L $^{-1}$ , Dosskey and Bertsch, 1994; Novak and Burras, 1994) and frequent flooding reduces organic residue decomposition (Daniels et al., 1999). In this studied wetland, the SedOC contents ranged between 6.9 and 90.9 g kg $^{-1}$  (Table 1). The sediments were also mildly acidic, with pH values ranging between 5.6 and 6.4. Their TP and  $P_{\rm max}$  values ranged between 52 and 471 and from 187 to 633 mg kg $^{-1}$ , respectively. In most cases, the sediments had higher concentrations of oxalate-extractable Al than Fe and higher pyrophosphate-extracted Al, Fe, and Ca than Mg and Mn (Table 2).

## Regression Analyses between Sediment Organic Carbon, Phosphorus Sorption Maximum, and Total Phosphorus Values

There was a significant relationship (both linear and exponential) between the in-stream wetland SedOC contents, and TP concentrations (Fig. 2a), and between SedOC

Table 1. Chemical properties, including pH, sediment organic C (SedOC), total P (TP), and the P sorption maxima ( $P_{max}$ ) of sediments.

| Site | Year | Sample no. | pН  | SedOC                        | TP   | P <sub>max</sub> |
|------|------|------------|-----|------------------------------|------|------------------|
|      |      |            |     | $\mathrm{g}\mathrm{kg}^{-1}$ | — mg | -1               |
| 1    | 1997 | 1          | 6.0 | 18.7                         | 91   | 326              |
| 1    | 1998 | 2          | 6.1 | 6.9                          | 46   | 252              |
| 1    | 1999 | 3          | 6.0 | 9.8                          | 81   | 192              |
| 2    | 1997 | 4          | 5.7 | 90.9                         | 471  | 575              |
| 2    | 1998 | 5          | 5.7 | 42.6                         | 181  | 641              |
| 2    | 1999 | 6          | 5.9 | 60.6                         | 284  | 617              |
| 3    | 1997 | 7          | 5.6 | 20.1                         | 128  | 405              |
| 3    | 1998 | 8          | 6.1 | 15.9                         | 120  | 346              |
| 3    | 1999 | 9          | 6.4 | 8.1                          | 115  | 210              |
| 4    | 1997 | 10         | 6.3 | 9.0                          | 52   | 258              |
| 4    | 1998 | 11         | 5.8 | 43                           | 189  | 578              |
| 4    | 1999 | 12         | 6.1 | 30                           | 163  | 525              |

and  $P_{\rm max}$  values (Fig. 2b). Likewise, variations in the instream wetland SedOC concentrations also significantly influenced  $P_{\rm max}$  values, but the relationship was more strongly exponential ( $r^2=0.90$ ) than linear ( $r^2=0.41$ , P=0.07). The exponential relationship implies that the sediments  $P_{\rm max}$  values are significantly linked to SedOC contents, especially below 60 g kg $^{-1}$  (Fig. 2b, P<0.001). The curve begins to reach a plateau at about 625 mg P kg $^{-1}$  suggesting that the OC structures associated with the sediments in this wetland have reached an upper P binding threshold capacity. These two significant relationships shown in Fig. 2a and 2b support the conclusion that P binding (as  $P_{\rm max}$ ) and accumulation (as TP) in this in-stream wetland are both dependent on the SedOC content.

The hypothesis concerning a connection between the SedOC and its TP concentrations was made assuming that a positive relationship also existed between the sediments  $P_{max}$  and TP values. If the sediments  $P_{max}$  value increased, then potentially more P can be bound, thus causing P accumulation into the TP pool. For this instream wetland, regression analyses showed that the sediments P<sub>max</sub> concentrations accounted for 53% of the differences in their TP values (Fig. 3). Although only 53% of the variability was explained, the positive linear relationship between these two variables was significant (P = 0.01). The finding is similar to results of Wang et al. (2005) who reported a significant (P < 0.01) relationship between sediment  $P_{\text{max}}$  and TP concentrations for 11 sediments collected from the middle and lower reaches of the Yangtze River in China.

Table 2. Oxalate- and pyrophosphate-extractable cation concentrations from sediments.

| Sample no. | Alox | Fe <sub>ox</sub> | Alpyro | Capyro | Fepyro | $Mg_{pyro}$ | Mnpyro |
|------------|------|------------------|--------|--------|--------|-------------|--------|
| '          |      |                  |        |        |        |             |        |
| 1          | 922  | 762              | 591    | 272    | 545    | 70          | 15     |
| 2          | 388  | 898              | 322    | 200    | 363    | 25          | 11     |
| 3          | 455  | 347              | 335    | 184    | 321    | 26          | 7      |
| 4          | 4558 | 1346             | 3153   | 1285   | 174    | 253         | 22     |
| 5          | 2113 | 660              | 1760   | 461    | 591    | 115         | 12     |
| 6          | 1623 | 1154             | 1350   | 745    | 1471   | 125         | 17     |
| 7          | 1188 | 531              | 867    | 427    | 752    | 63          | 16     |
| 8          | 1650 | 404              | 881    | 293    | 277    | 89          | 15     |
| 9          | 981  | 227              | 492    | 332    | 286    | 62          | 16     |
| 10         | 477  | 180              | 386    | 137    | 267    | 25          | 10     |
| 11         | 1812 | 432              | 1627   | 398    | 594    | 100         | 11     |
| 12         | 1882 | 130              | 1814   | 251    | 209    | 112         | 16     |

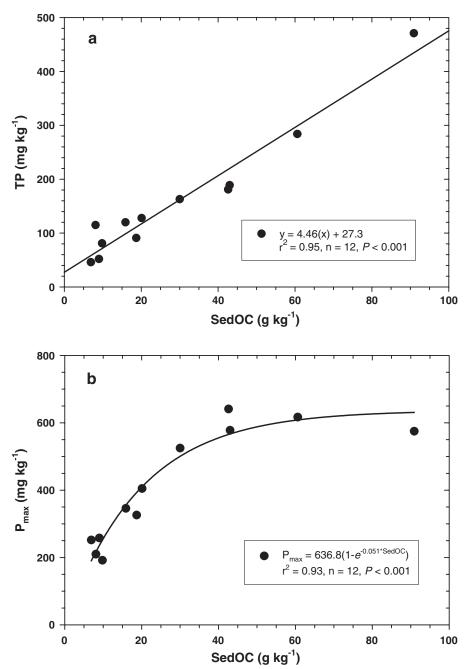


Fig. 2. Regression relationships between sediment organic C (SedOC) concentrations and (a) total P (TP) and (b) P sorption maxima (Pmax) values.

## Cation Concentration Relationships with Phosphorus Sorption Maxima, and Total Phosphorus Values

## **Oxalate-Extracted Cations**

Amorphous and poorly crystalline forms of oxalate-extractable Al and Fe have been statistically linked with  $P_{\rm max}$  values in soils and sediments (Khalid et al., 1977; Richardson, 1985; Gale et al., 1994). Therefore, sediment samples were extracted using an oxalate reagent and regression relationships were determined for Fe $_{\rm ox}$  and Al $_{\rm ox}$  with TP and  $P_{\rm max}$  concentrations. There was a highly significant ( $r^2=0.87,\,P<0.001$ ) linear rela-

tionship between sediment TP and  $Al_{\rm ox}$  concentrations (Fig. 4a). Thus, the sediment  $Al_{\rm ox}$  content is a good predictor for TP concentrations within this particular instream wetland because it explains 87% of the variability between these variables. On the other hand, Fe<sub>ox</sub> concentrations were a poor predictor of the sediment TP contents because it only accounted for 46% of the variability (Fig. 4b). When using the combination of  $Al_{\rm ox}$  + Fe<sub>ox</sub> concentrations as a treatment variable, however, the statistical relationship with TP was greatly improved ( $r^2 = 0.92$ , P < 0.001, data not shown).

The  $Al_{ox}$  concentrations were significantly correlated with  $P_{max}$  values (Fig. 4c), and the exponential model

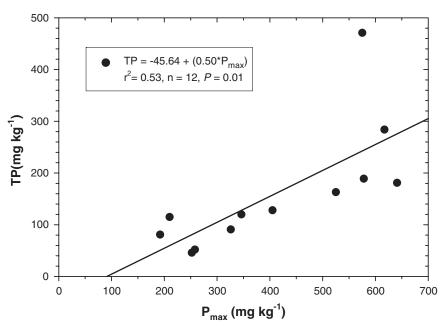


Fig. 3. Regression relations between P sorption maxima ( $P_{max}$ ) and total P (TP) values.

explained 78% of the variation in P<sub>max</sub> values among the 12 sediment samples. In contrast, linear regression revealed a poor relationship ( $r^2 = 0.19$ ) between the Fe<sub>ox</sub> concentrations and the sediment P<sub>max</sub> values (Fig. 4d). Applying an exponential model to these variables did not improve the statistical relationship (data not shown). The lack of a significant relationship between P<sub>max</sub> and the sediment Fe<sub>ox</sub> contents is contrary to the reports of Shukla et al. (1971) and Khalid et al. (1977). Both of these researchers reported that Fe<sub>ox</sub> concentration was the single most important criterion explaining P sorption in noncalcareous sediments. This contrary finding may be a result of the majority of oxides and hydroxides being formed from Al<sup>+3</sup> instead of Fe<sup>+3</sup> because significantly more Al was extracted with oxalate (Table 2, pooled mean =  $1479 \text{ mg kg}^{-1}$ , SD =  $147 \text{ mg kg}^{-1}$ , t-test, P < 0.05) from the sediments compared to Fe (pooled mean =  $589 \text{ mg kg}^{-1}$ , SD =  $388 \text{ mg kg}^{-1}$ ). Additionally, lower Fe concentrations in wetland sediments may be the result of conversion of Fe<sup>+3</sup> into the more soluble Fe<sup>+2</sup> form during periods of chronic flooding, which can be lost with outflowing water (Hogan et al., 2004). Using the combination of  $Fe_{ox} + Al_{ox}$  slightly improved the fit with  $P_{max}$  ( $r^2 = 0.49$ , P = 0.05, data not shown) relative to the results obtained using only Fe<sub>ox</sub> concentrations (Fig. 4d).

## **Pyrophosphate-Extracted Cations**

Five different pyrophosphate-extractable cations (Al, Fe, Ca, Mg, and Mn) were selected for this evaluation because they are among the most common suite complexed by humic substances and develop relatively strong coordinate complexes (Stevenson, 1994). The concentration of four of the five cations were all linearly dependent on the SedOC content (Table 3,  $r^2 \ge 0.80$ , P < 0.001). This confirms the hypothesis that, as the SedOC

content increases, there is a concomitant linear rise in the concentration of this suite of chelated cations. The  $\beta$  values for the extractable cations were  $Al_{pyro} > Fe_{pyro} > Ca_{pyro} > Mg_{pryo}$  and fit the order of metal binding by organic ligands (Stevenson, 1994). Trivalent cations are bound to a greater extent than divalent ones and can form stronger coordination complexes with organic ligands (Stevenson, 1994). While still significant, the Mn concentrations were poorly predicted (41%) with SedOC contents, which may simply be due to the low Mn concentrations complexed by SedOC (lowest  $\beta$  in Table 3).

A combination of linear, multiple linear, and exponential regression equations were used to identify relationships between concentrations of individual and sets  $(X_{\rm pyro}, Y_{\rm pyro})$  of chelated cations with both the sediment  $P_{max}$  and TP concentrations (Table 4, Fig. 5). The highest  $r^2$  and most significant P value through linear regression were obtained between P<sub>max</sub> and Al<sub>pyro</sub>. Variations in  $Al_{pvro}$  explained 67% of the variability in  $P_{max}$ , whereas none of the remaining pyrophosphate-extracted cations explained >54% of the variability. The prediction capability between P<sub>max</sub> and Al<sub>pyro</sub> was improved to 88%, however, when an exponential equation was fitted to the data (Fig. 5a). Applying the exponential equation to the other four pyrophosphate-extractable cations did not significantly improve the fit (data not presented) compared with linear results. When multiple linear regressions were applied between P<sub>max</sub> and sets of pyrophosphate-extractable cations, multicollinearity often occurred. Multicollinearity means that changing the parameters of either of two variables had a similar effect on the fit, which made estimates of regression coefficients and P values unreliable (SPSS, 2005).

Linear regression results between the sediments TP concentrations and Al<sub>pyro</sub>, Ca<sub>pyro</sub>, and Mg<sub>pyro</sub> were all highly significant (P < 0.001) and had  $r^2$  values between 0.79 and 0.94 (Table 4). Statistical results between Fe<sub>pyro</sub>

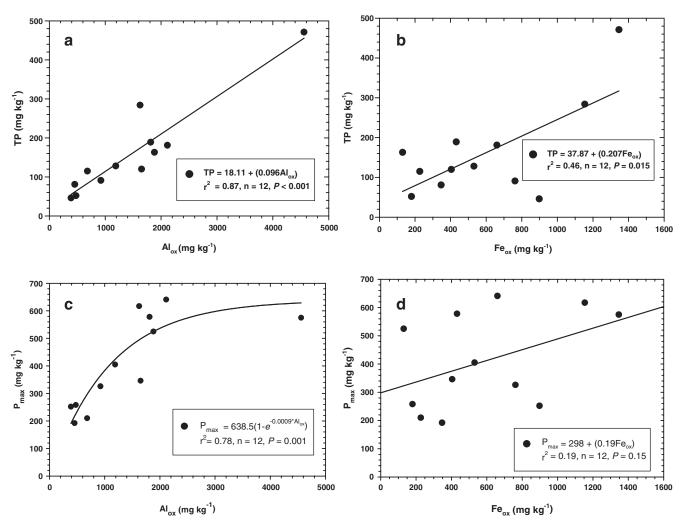


Fig. 4. Regression relations between total P (TP) and (a) oxalate-extractable Al ( $Al_{ox}$ ) and (b) oxalate-extractable Fe ( $Fe_{ox}$ ) concentrations and P sorption maxima ( $P_{max}$ ) concentrations with (c)  $Al_{ox}$  and (d)  $Fe_{ox}$ .

or  $Mn_{pyro}$  and TP concentrations were slightly lower than the other three pyrophosphate-extracted cations. The data showed that  $Al_{pyro}$ ,  $Ca_{pyro}$ , and  $Mg_{pyro}$  were correlated with TP concentrations; therefore, multiple regression analyses were used to distinguish relationships between multiple sets of these three cations. Significant results were obtained only when  $Al_{pyro}$  and  $Ca_{pyro}$  concentrations together were regressed against their respective TP contents (Fig. 5b), while multicollinearity was obtained in all other sets. Using the combination of  $Al_{pyro}$  and  $Ca_{pyro}$  concentrations in a multilinear regression relationship explained 98% of the variability in TP concentrations within this studied wetland.

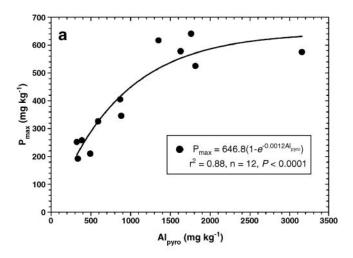
Table 3. Variables from the regression equations between sediment organic C (SedOC) and pyrophosphate-extracted cation concentrations in sediment.

| Cation   | β    | y intercept         | $r^2$ | P       |
|----------|------|---------------------|-------|---------|
|          |      | mg kg <sup>-1</sup> |       |         |
| Al       | 30.3 | 229                 | 0.85  | < 0.001 |
| Ca       | 11.5 | 72                  | 0.87  | < 0.001 |
| Fe       | 17.1 | 108                 | 0.80  | < 0.001 |
| Mg       | 2.29 | 20                  | 0.89  | < 0.001 |
| Mg<br>Mn | 0.09 | 11                  | 0.41  | 0.024   |

The strong involvement of Ca with TP concentration in this study is contrary to Stevenson (1994), who reported that Fe forms a stronger coordination complex with organic ligands. It may be possible that chelated Ca involvement with P binding has been understated. The statistical results suggest that complexed Ca has a strong role in TP accumulation within this wetland, which is supported by its higher  $\beta$  value than  $Al_{pyro}$  and  $Fe_{pyro}$  (Table 4). In a complex mixture of multivalent cations,

Table 4. Linear regression results for relationships of P sorption maxima ( $P_{max}$ ), and total P (TP) with pyrophosphate-extractable cation concentrations.

|   | β     | y intercept         | $r^2$ | P       |
|---|-------|---------------------|-------|---------|
|   |       | mg kg <sup>-1</sup> |       |         |
| Pmax vs. Alpvro                         | 0.16  | 220.54              | 0.67  | < 0.001 |
| P <sub>max</sub> vs. Ca <sub>pyro</sub> | 0.31  | 269.62              | 0.37  | 0.034   |
| P <sub>max</sub> vs. Fe <sub>pyro</sub> | 0.21  | 276.51              | 0.36  | 0.036   |
| P <sub>max</sub> vs. Mg <sub>pyro</sub> | 1.95  | 230.46              | 0.53  | 0.007   |
| P <sub>max</sub> vs. Mn <sub>pyro</sub> | 18.95 | 137.44              | 0.20  | 0.141   |
| TP vs. Al <sub>pyro</sub>               | 0.13  | 16.42               | 0.83  | < 0.001 |
| TP vs. Capyro                           | 0.36  | 10.1                | 0.94  | < 0.001 |
| TP vs. Fe <sub>pyro</sub>               | 0.21  | 28.25               | 0.79  | < 0.001 |
| TP vs. Mg <sub>pyro</sub>               | 1.82  | -1.16               | 0.93  | < 0.001 |
| TP vs. Mn <sub>pyro</sub>               | 21.91 | -147.39             | 0.54  | 0.006   |



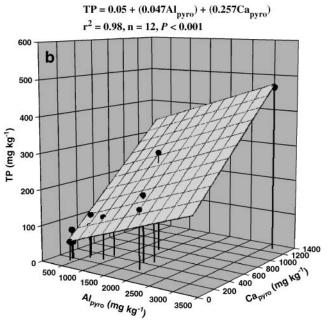


Fig. 5. Regression relations between (a) phosphorus sorption maximum  $(P_{max})$  and pyrophosphate-extractable Al (Al $_{pyro}$ ) concentrations and (b) TP and Al $_{pyro}$ + pyrophosphate-extractable Ca (Ca $_{pvro}$ ).

however, it would be expected that Ca, which forms weaker coordination complexes with organic molecules, should be easily displaced by Al and Fe ions (Stevenson, 1994). In spite of the slightly acidic pH values of the sediments, these results suggest that the Ca present in this in-stream wetland was capable of forming complexes in the presence of both Al and Fe. The ability of chelated Ca to bind P in the presence of Al and Fe may be due to shifts in their overall charge from trivalent into dimeric (AlOH<sup>+2</sup>, FeOH<sup>+2</sup>) and monomeric [Al(OH)<sub>2</sub><sup>+</sup>, Fe(OH)<sub>2</sub><sup>+</sup>] forms caused by sediment pH differences (Bohn et al., 1979). Formation of lower charged Al and Fe cationic species probably decreases their ability to compete with Ca for chelation sites on the organic molecules. As more Ca is chelated by organic structures in the SedOC pool, P binding would be enhanced because the negatively charged binding site would have acquired more of a positive charge. As the binding site acquires more

positive charge, additional P will be electrostatically attracted to the chelated Ca at this site (Barrow, 1972).

## **CONCLUSIONS**

The P binding ability of wetland sediments has been traditionally linked to their  $Al_{ox}$  and  $Fe_{ox}$  concentrations. Alternatively, several reports have suggested that cations chelated by organic ligands can also bind P; however, the involvement of specific cations or sets of cations in this process is largely unknown. The objectives of this study were to define the role of organically complexed cations in P binding by sediments and to statistically determine the most influential pyrophosphate-extracted cations on P binding and accumulation. Traditional extraction of sediments to measure Al and Fe concentrations using oxalate and their involvement in P binding and accumulation were also performed as a comparison with results obtained using pyrophosphate.

Similar to results obtained by other researchers for soils and sediments, the sediment  $P_{\rm max}$  and TP values were significantly linked to the wetland's SedOC contents. This finding is substantial because it exemplifies the important role that SedOC has with binding and accumulating P. Wetlands need to store P to reduce P loads transported into coastal bays and estuaries. Results from this study indicate that more P can be stored in the wetland as TP when the sediments have high  $P_{\rm max}$  and SedOC contents.

Cations complexed by SedOC were strongly involved with both  $P_{\rm max}$  and TP concentrations; however, some cations had a stronger influence than others. Statistical analyses revealed that 88% of the variability in the sediment  $P_{\rm max}$  values was explained by  $Al_{\rm pyro}$  concentrations. A better relationship was obtained when the combination of  $Al_{\rm pyro}$  and  $Ca_{\rm pyro}$  was regressed with the sediment TP concentrations. In the presence of multiple cations, chelated Ca and Al had a pronounced influence on the sediment TP concentrations. In fact, statistical analyses revealed that chelated Ca had a more important role in TP binding in this wetland than complexed Fe, Mg, or Mn.

Oxalate-extractable Al also had a significant influence on the sediment  $P_{max}$  and TP concentrations. In contrast, poor predictive results were obtained when  $Fe_{ox}$  concentrations were used alone. Aluminum's more significant role in P binding, compared with Fe, is similar to other studies (Darke and Walbridge, 2000; Hogan et al., 2004). Iron still has a role in P binding, however, because when  $(Al_{ox} + Fe_{ox})$  concentrations were combined, the prediction of TP concentrations was greatly improved.

Maximizing P storage in wetlands requires an understanding of P binding pathways that reduce P concentrations in the water column. This study revealed that cations associated with amorphous and poorly crystalline phases as well as those chelated by SedOC are important in P binding. Although it was not possible to discern the individual importance between these two P binding processes, the results highlight that both are inextricably linked with the ability of this wetland to sorb P.

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